



The latest advancements on thermochemical heat storage systems



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ABSTRACT

Thermal energy storage (TES) is an advanced technology that could address the energy supply-demand balance in building air conditioning systems. TES is also important in view of the increasing utilisation of solar energy. Although sensible heat storage systems and latent heat storage systems have been heavily researched and are widely used domestically and industrially, thermochemical heat storage (THS) systems are currently undergoing a surge in research and development. Recent studies suggest that THS has significant advantages when compared with the other heat storage methods including higher storage density, lower volume requirements, low heat loss (approaching zero), and lower charging temperature. On the other hand the complexity and higher investment costs remain the main obstacles to rolling out these systems commercially. A comprehensive review has been presented here into all aspects of the current, state of the art THS research. It includes comparisons with other storage methods, description of absorption/adsorption cycles, the materials used in these systems and open/closed storage methods, as well as chemical heat pumps. Recent advances in the field are also investigated and discussed.

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1. Introduction

Due to increases in worldwide human population, technological development, and industrialisation, usage of fossil fuels has been dramatically rising. Added to this, the rise in greenhouse gas

Abbreviations: CHP, chemical heat pump; HAM, heat and mass transfer; HP, heat pump; LHS, latent heat storage; PCM, phase change material; SHS, sensible heat storage; STES, sorption thermal energy storage; TES, thermal energy storage; THS, thermochemical heat storage

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emissions and fuel prices have contributed to the well-established development of various renewable energy resources such as wind, solar, tidal and geothermal etc. However there remains a mismatch between most renewable energy supplies and user demand which is currently one of the main barriers to both improving and implementation of successful sustainable energy systems [1]. Improving renewable energy systems and in particular energy storage systems to tackle this mismatch is arguably as important as developing new energy resources. Storage of energy in an appropriate way and developing systems to allow immediate availability in case of necessity should be the key aim for today's energy researchers, to provide that equilibrium between supply and demand.

Solar energy is currently seen as one of the most promising alternatives to conventional energy resources. The use of solar thermal energy has been widely researched, publicly accepted and implemented for heating, ventilation and air-conditioning in both domestic and industrial settings. Pareweshwaran et al. demonstrated that the highest total energy usage takes place in the domestic sector [2]. Over half of the energy consumed in the domestic sector is for space heating/cooling and hot water purposes [2]. Despite the common acceptance of solar thermal systems, the main obstacle in its application is the mismatch between the supply and demand. Development of reliable and economically feasible thermal storage systems is of vital importance for the efficient and sustainable use of solar energy into the future.

Currently, there are three main types of thermal energy storage technologies available:

1. Sensible heat storage (SHS).
2. Latent heat storage (LHS). SHS and LHS are employed both on a small scale for heating purposes in buildings and on a larger scale in solar thermal power plants [2].
3. Thermochemical heat storage (THS) is a relatively new technology with much research and development on these systems ongoing.

Among these storage techniques, THS appears to be a promising alternative to be used as an energy storage system [3–5]. THS

systems can utilise both sorption and chemical reactions to generate heat and in order to achieve efficient and economically acceptable systems, the appropriate reversible reactions (suitable to the user demand needs) need to be identified [3–6]. In recent years, sorption thermal energy storage (STES) systems coupled with chemical systems are increasingly gaining credibility as they become promising options for solar heat storage [3–6]. Their advantages include relatively high storage capacities and the unique function to preserve energy for longer periods with limited heat loss.

The aim of the present review is to evaluate the current situation of THS systems research and implementation as well as to highlight the main deficiencies of the current systems that stand in the way of proper commercialisation. A general evaluation and comparison of the current research on heat storage systems and materials has also been provided.

2. Thermochemical heat storage

For comparison, the physical and chemical properties of the most promising materials used in LHS, SHS and THS systems are given in Table 1. Using these values, the energy storage density, E_d of these materials was calculated and is presented in Fig. 1 with a graphical comparison.

THS materials have approximately 8–10 times higher storage density over SHS, and two times higher over LHS materials when compared on a like for like storage volume basis. However in THS, there are limitations in that an efficient reaction requires efficient heat and mass (HAM) transfer to and from the storage volume. This condition can severely limit the overall storage volume which is not the case in SHS and LHS systems, allowing higher volumes to be utilised. This volume limitation due to the HAM transfer characteristics is one of the key areas for current research in order to deliver effective THS or TES systems in the future.

The average monthly heat load of a typical 100 m² domestic building in UK is in the range of 1037 kW h (October)–2101 kW h (January). Using these values a comparison of heat load coverage ratios of different the heat storage materials for each month was analysed (see: Table 2 and Fig. 2). The analysis was carried out using a nominal 1 m³ storage volume. The results show that with the same storage volume, THS provides the highest heat storage followed secondly by LHS. With THS and LHS it is possible to meet

Table 1
Physical and chemical properties of the most promising heat storage materials.

	Material	Density (kg/m ³)	Specific heat capacity (kJ/kg)	Latent heat of fusion (kJ/kg)	Reaction enthalpy (kJ/kg)
Sensible	Rock	2240	0.9	–	–
	Sandstone	2200	0.71	–	–
	Brick	1600	0.84	–	–
	Soil	1300	0.46	–	–
	Concrete	2240	1.13	–	–
Latent	Paraffin wax	1802	–	174.4	–
	CaCl ₂ · H ₂ O	2100	3.06	–	433.6
Thermochemical	Zeolite	650	1.07	–	1107
	Silica gel	600	1.13	–	1380

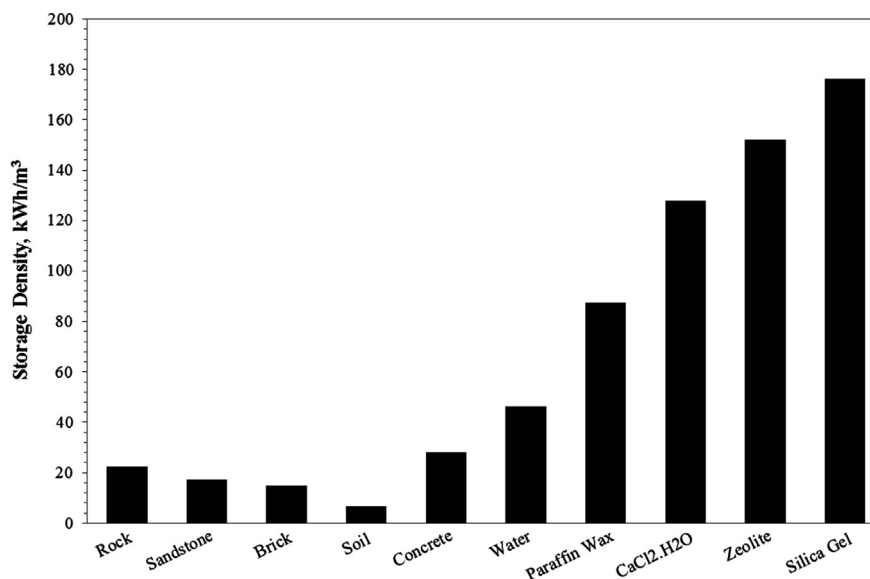


Fig. 1. Comparison of heat storage densities of different materials.

around 10% and 5% of heat load (4–6 kW) respectively. However this is less than 1% for sensible storage methods such as soil, sandstone and concrete for 1 m³ storage volume.

LHS systems can have phase change processes from solid to liquid, liquid to gas or the inverse of these processes [7–12]. There are several studies about LHS and SHS in the literature. Combining these heat storage systems with solar collectors and heat pumps can bring significant advantages for decreasing energy consumption. Some of the previous studies about hybrid heating systems are listed in Table 3.

Thermochemical heat storage (THS) has the distinctive advantages of coupled high energy storage and low heat losses when compared to both SHS and LHS technologies and is currently

regarded as the most promising alternative [3,24,25]. Another attractive property of THS is its capability of the systems to conserve the heat energy at ambient temperature as long as desired without heat losses due to their reversible chemical reactions. Due to the advantages mentioned above, THS has become a widely researched technology for seasonal energy storage [25]. Fig. 3 illustrates a comparison of the energy densities of some high energy storage materials.

The effective performance of a THS system depends on several design parameters are all vital for achieving a high system temperature lift, ΔT .

- THS material
- Ambient psychrometric conditions where the storage system will be used
- Process design
- Reactor design

THS systems can be further classified as either solely chemical or thermochemical reaction storage. Chemical storage systems are based on a reversible reaction of two separate chemical substances where a high amount of energy is generated as a result of an exothermic synthesis reaction. Thermochemical reaction storage systems on the other hand are related to sorption mechanisms. Within a sorption system a relatively small amount of energy with a lower temperature is generated, however there is a lower

Table 2
Heat load coverage ratios of various heat storage materials in UK conditions during 6 month heating period.

	Sandstone (%)	Soil (%)	Concrete (%)	Paraffin (%)	CaCl ₂ (%)	Silica gel (%)	Zeolite (%)
October	1.6	0.6	2.7	8.4	12.3	17.0	14.7
November	1.2	0.4	2.0	6.1	9.0	12.4	10.7
December	1.0	0.3	1.7	5.2	7.6	10.5	9.0
January	0.8	0.3	1.3	4.2	6.1	8.4	7.2
February	1.0	0.4	1.8	5.4	8.0	11.0	9.5
March	1.1	0.4	1.9	5.9	8.6	11.8	10.2

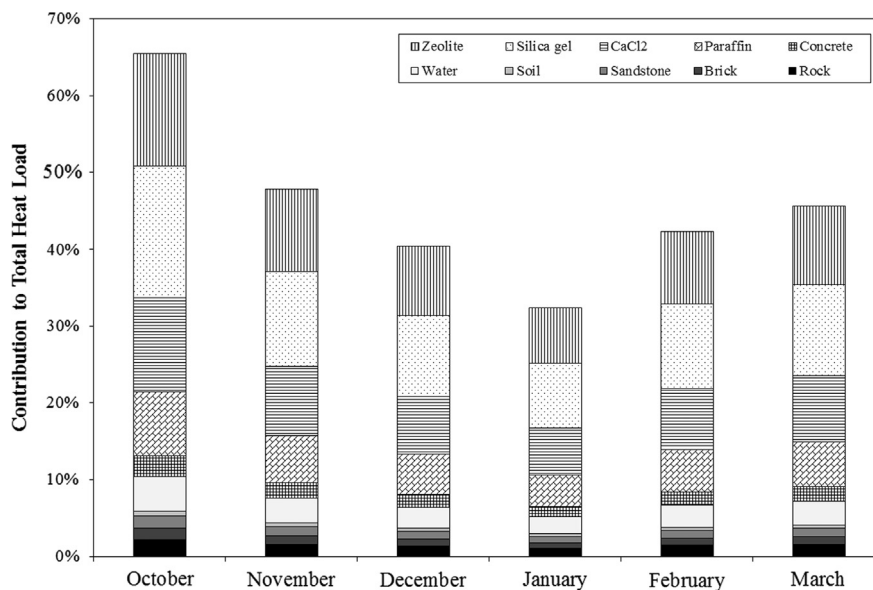


Fig. 2. Comparison of heat load coverage ratios of various heat storage materials in UK conditions during a 6 month heating period (October–March).

Table 3
Previous studies researching hybrid heating systems.

	Type of study	Material	Heat storage method	Other components	η_i	η_{II}	COP
Koca et al. [13]	Exp.	CaCl ₂ · 6H ₂ O	LHS	Flat plate solar collector	45%	2.2%	–
Ozturk et al. [14]	Exp.	Paraffin	LHS	Flat plate solar collector	40%	4.2%	–
Hussain et al. [15]	Num.	Ethylene glycol	SHS	HVAC	80%	0.5–14%	–
Benli et al. [16]	Exp.	CaCl ₂ · 6H ₂ O	LHS	GSHP	–	–	2–3.5
Kumari et al. [17]	Exp.	CaCl ₂ · 6H ₂ O	LHS	–	–	–	–
Han et al. [18]	Num.	CaCl ₂ · H ₂ O	LHS	Solar collectors+HP	–	–	3.3–6
Wang et al. [19]	Exp.	Soil	SHS	Solar collectors+HP	–	–	6.6
Wang et al. [20]	Exp.	Water	Underground SHS	Solar-ground source heat pump	76%	–	–
Fernandez-Seara et al. [21]	Exp.	Water	SHS	Solar collectors+HP	–	–	3.2
Günerhan and Hepbasli [22]	Exp.	Water	SHS	Solar collectors	–	3.3–4.4%	–
Bascetincelik et al. [23]	Exp.	Paraffin	LHS	Solar collectors	42%	3.3%	–
Utlü et al. [9]	Exp.	Paraffin	LHS	Solar collectors+GSHP	62–74%	7–37%	–

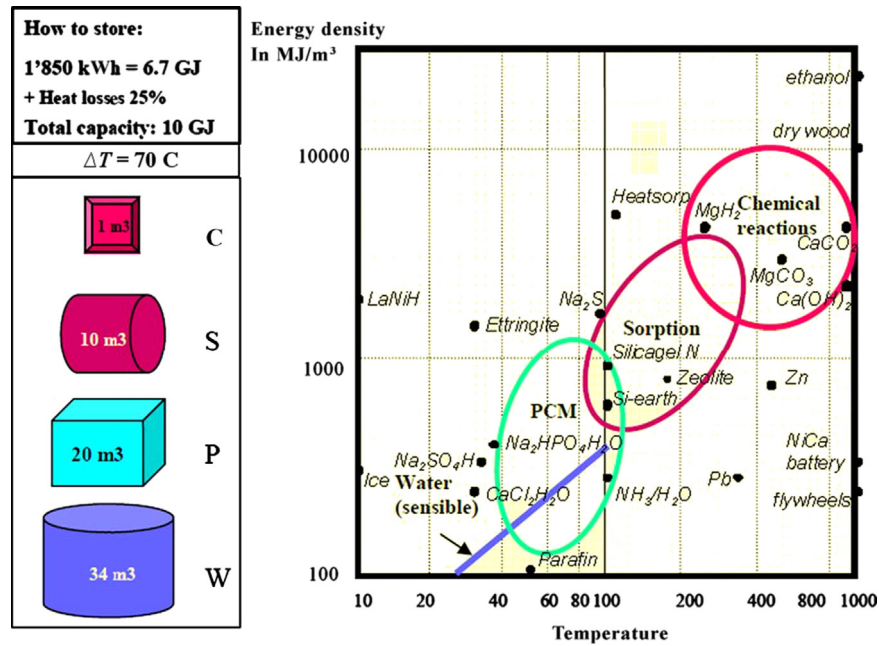


Fig. 3. Comparison of energy storage densities of energy storage methods. Adapted from: [25,103].

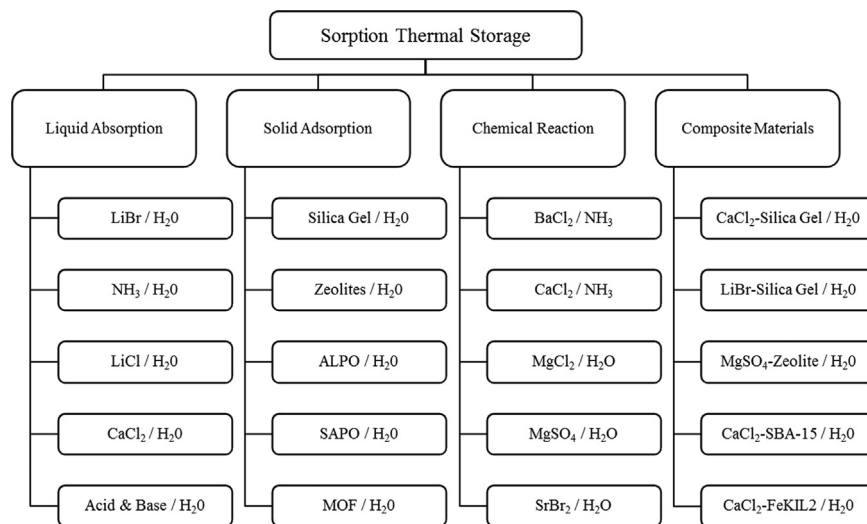


Fig. 4. Sorption thermal storage methods and materials [26].

activation energy required to start the reaction. This provides sorption storage systems with an advantage over solely chemical systems for low temperature applications. Fig. 4 illustrates most promising sorption storage materials.

The characteristics of sorption process are [26];

- They require heat to expel a sorbate (gas) from the sorbent (matrix)
- No sorption process can take place until there is contact between the sorbent and sorbate. With hermetic isolation of the sorbate, thermochemical energy can be stored independent of the time.
- There is no heat or entropy loss during storage allowing long term storage with THS.
- Solar energy can be stored during the summer (charging/desorption) to meet heating demand in winter (discharging/sorption).
- LHS can only be applied for specific temperatures ranges whereas THS has greater flexibility for determining both input

and output temperatures allowing a greater range of practical applications.

- THS can also be applied either during the summer for cooling (charging) or in the winter for heating (discharging).

According to the system design, sorption thermal storage systems can be divided into either 'open' or 'closed' systems.

2.1. Open sorption systems

Open systems, as the name suggests are open to the environment. The sorbate used (typically water vapour) for the sorption process during discharging is obtained directly from the ambient air or, in some cases from a moisture source such as a humidifier. In summer solar energy can be used to separate the adsorbed water from the absorbent. Compared with closed cycles, open storage systems have an easier process design which makes operational conditions easier. However, because the vapour adsorption/heat

generation and heat transfer to air take place at the same time, reactor design is vital for storage performance. Providing a moisture adsorption for a longer time is directly related with the air temperature lift, ΔT . Although at the beginning of the reaction, there is good vapour diffusion within these systems, as the time passes, the diffusion shows a decreasing trend and results in a corresponding drop in ΔT . This causes instability during heat generation, which is not evidenced in closed sorption systems. In closed cycles, the generated heat can be stored sensibly and the amount extracted can be altered by changing the parameters of the heat transfer fluids (e.g. mass flow rate).

2.2. Absorption cycles

Absorption (see: Fig. 5) is the penetration of the adsorbate through the surface layer of an absorbent with a change of composition [27]. Absorption heat pump (AHP) technology has been further developed when compared to adsorption heat pumps [28,29]. This is primarily due to the fact that the absorption cycle is more suitable for low grade heat utilization [30–34]. Some of the most promising sorbent/sorbate couples for absorption cycles are water–lithium bromide (H_2O – LiBr) and ammonia–water (NH_3 – H_2O) [27–29].

In order to improve the sorption properties of the AHP process, a new group of composite sorbent materials have recently been developed called ‘Salt In porous Matrix’ (SIM) [33,34,36–38]. They have been utilized for sorption cooling, heat pumps and heat storage applications. Tanashev et al. [36] developed a composite inorganic salt in a porous matrix where CaCl_2 , MgCl_2 and LiBr were confined to the pores of silica gel and alumina as the porous matrix. A mathematical model was investigated for analysis of the thermal conductivity of these composites, dependant on their water uptake.

If water is used as a sorbate, these materials are termed ‘Selective Water Sorbents’ (SWS) [37,38]. There are two component

parts to each SWS – one component is a host matrix (i.e. silica gel, alumina, expanded vermiculite, aerogel) the other is an inorganic salt (i.e. LiCl , CaCl_2 , MgCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, LiNO_3) which is placed inside the matrix pores [37–42]. The host matrix has significant importance on the overall adsorption mechanism. The matrix serves to both hold the adsorbent and prevent dispersion of it. Also some of the host matrices can enhance HAM transfer due to the increased surface area and increase performance of the salt/sorbate reaction. The characteristic properties for some of the most promising host matrices are given in Table 4. The sorbate (water vapour) sorption process (see: Fig. 6) contains two main mechanisms, (i) a chemical reaction between the salt and sorbate and (ii) liquid absorption [35–43].

2.3. Chemical heat pumps

The benefit of a suitable heat pump coupled to a low-temperature heat source is that it can upgrade that heat to a higher temperature. This is commonly achieved by consumption of electricity in the case of vapour compression heat pumps whilst chemical heat pumps (CHP) do not require electric power since mechanical compression is not required in the system. Although conventional heat pumps are used commercially [9], several research studies have been undertaken on chemical heat pumps because of their significant advantages in terms of energy consumption. Sharonov and Aristov [45] developed an analysis technique to identify the ideal cycle of both chemical and adsorption heat pumps in order to compare their performance. It was shown that for chemical heat pumps it was possible to reach Carnot efficiency however adsorption heat pumps have a lower efficiency due to entropy generation. Kato et al. [46] carried out a performance analysis of a packed bed reactor CHP. In this study the exhaust gas of a diesel engine was used for the desorption process.

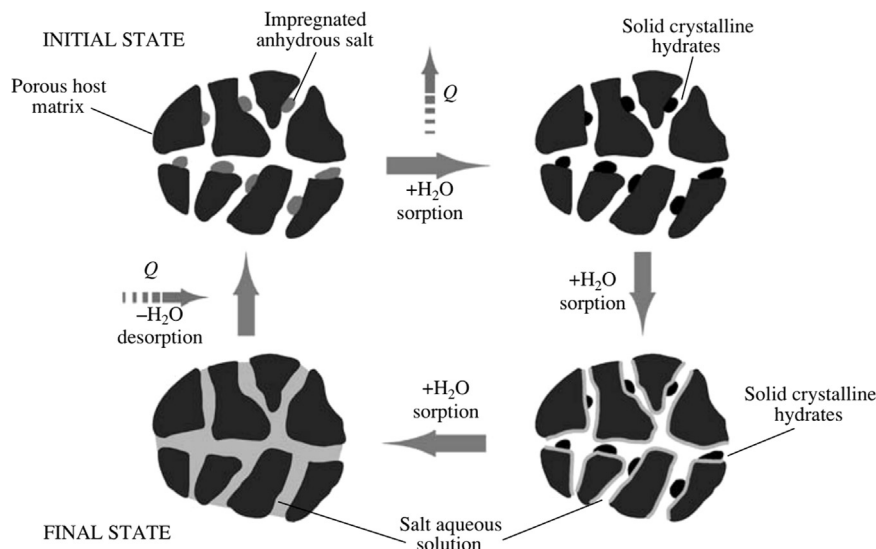


Fig. 5. Water sorption mechanisms on salt [26,35].

Table 4
Comparison of the characteristic properties of the most promising host matrices.

	Symbol	SSA (m ² /g)	V _p (cm ³ /g)	ρ_{bulk} (kg/m ³)	C _p (kJ/kgK)	W _{sat} (%)	λ (kW/mK)	T _r (°C)	Cost (\$/kg)
Vermiculite	(MgFeAl) ₃ (AlSi) ₄ O ₁₀ (OH) ₂ ·4(H ₂ O)	8–10	2.8	64–160	0.84–1.08	20–50	0.064	50–80	0.21–44
Silica gel	SiO ₂	750–850	1	480–720	1.13	30–40	0.174	130–150	0.88–1.34
Zeolite	Na[(AlO ₂)(SiO ₂)]0.2(H ₂ O)	550–600	0.17	1000–1120	1.08	40–75	0.07	> 200	1.65–2.2
Activated carbon	C(AC)	1500–1700	2	2000–2100	1.06	50	0.15–0.5	150–180	0.5–5
Expanded natural graphite	C(ENG)	18–22	0.073	1200–1500	0.7	40–60	6–8	100–200	1.8–2.5
Activated alumina	Al ₂ O ₃	150–300	44	750–1000	1	60	1.4–2.5	160–220	0.98–1.65

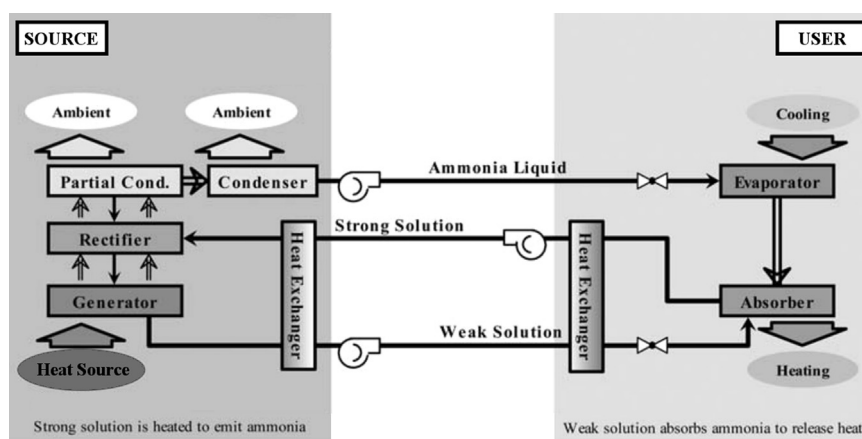


Fig. 6. Schematic diagram of a low grade heat absorption cycle [44].

Kim et al. [47] developed a new material to enhance the reactivity and conductivity of $\text{MgO}/\text{H}_2\text{O}$ pair. CaCl_2 , Expanded graphite and magnesium hydroxide were used in the mixture. Also CaCl_2 was introduced into the mixture to improve vapour diffusivity during the hydration process. The mixture showed improved performance when compared with pure $\text{Mg}(\text{OH})_2$ and a $\text{Mg}(\text{OH})_2$ – CaCl_2 mixture. Flueckiger et al. [48] investigated the CHP performance with reversible endothermic reactions. A mass and energy analyses of the system was undertaken and it was found that the coefficient of performance (COP) and environmental impact of the system is comparable with alternative technologies such as mechanical compression heat pumps, however the exergy values were insignificant. As stated, CHP's require no electrical input for compression and for this reason they are expected to play an important role in the future utilization of solar/geothermal generated or waste heat.

CHP's consist, in principle, of two different chemical reactions each run at two different temperatures. The reaction sequence functions to upgrade thermal energy, with no theoretical consumption or production of chemicals. CHP systems consist of two main units, (i) an endothermic reactor (where low temperature heat is supplied) and (ii) an exothermic reactor (where high temperature heat is released). Also a condenser and an evaporator are used to condense or vapourise the adsorbate respectively [49–51]. A CHP can operate using either a gas–liquid absorption process or solid–gas adsorption process. Adsorption CHPs can be further classified into two groups [49–51];

1. Chemisorption CHP systems – these are driven by a chemical reaction occurring at the exposed surface that can be either electronic, ionic or covalent bonding.
2. Physisorption chemical heat pump – attraction is due to Van der Waals forces where the interaction energy is weak.

CHP systems involve endothermic desorption and exothermic adsorption/absorption processes. It is desirable to have an adsorbate/adsorbent pair or an absorbent/absorbate pair with high heat of adsorption/absorption to create a more efficient system. CHP absorption systems have been operating in industry, however according to Chua et al. [51], the commercial applications of the adsorption cycle are less common.

2.4. Thermochemical heat storage materials

Thermochemical heat storage (THS) systems have some great advantages when compared with the other storage systems such as high energy storage density, low volume requirement and low heat loss. Although there are still areas of THS's that have some weaknesses which are driving the current research, such as low

HAM transfer rates, low matrix permeability restricting sorbate access to and from the system and high pressure drops. These can all affect THS efficiency negatively. Many studies into absorption/adsorption materials as well as reactor design are currently being carried out to enhance mass transfer during the hydration process and also to enhance heat transfer during decomposition of the absorbate/adsorbate. Table 5 details some of the numerous methods currently being studied to enhance HAM transfer.

The reaction material or matrix is probably the key element of an entire THS system and should meet criteria as outlined in [25–26];

- High energy storage density (W h/kg or kW h/m^3)
- Low charging temperature
- High uptake of sorbate – compatibility of sorbent/sorbate
- Appropriate heat and mass transfer properties to ensure designed output power
- Easy to handle – non-poisonous.
- Low cost – low price per kW h heat energy stored.
- Thermal stability – no deterioration during cycling.

Of these, the sorption properties are the foundations to finding suitable THS materials for any given application, however the comprehensive evaluation of sorption properties of available sorbents is a time consuming task as it requires precise measurements of a set of sorption isobars, isosters and isotherms under a wide range of temperature of pressure. Evaluation of the materials energy density, E_d is somewhat more straight forward and reveals that metal chlorides, metal hydrides and metal oxides are considered to be promising materials for thermochemical heat storage systems [26]. The energy storage densities of some of the most promising sorbents are given in Fig. 7.

There are several studies in the literature detailing adsorbent/absorbent materials used as thermochemical storage material. Sole et al. [71] presented a study about the characterisation of adsorption materials (solid–gas) in order to obtain a reliable kinetic model. Different concepts when choosing a suitable material were evaluated and exemplified. Shkatulov et al. [72] developed a new composite material magnesium hydroxide, $\text{Mg}(\text{OH})_2$ /vermiculite. This material has a regeneration temperature of between 250–350 °C. It was synthesized by precipitation of $\text{Mg}(\text{OH})_2$ in the pores of expanded vermiculite. This composite has a maximum heat storage capacity 540 kJ/kg with a hydroxide content of 67.4%. It was reported that this amount of heat is higher than the latent heat of even the most promising phase change materials (PCM's).

Gordeeva et al. [43] investigated the phase composition of $(\text{LiCl} + \text{LiBr})/\text{SiO}_2$ composites and their sorption equilibrium with both methanol and water. It was reported that formation of a solid solution of LiCl in LiBr takes place in composites containing $\leq 25 \text{ mol}\%$

Table 5

Methods applied in previous studies to enhance HAM transfer in THS.

	Nature	Working pairs	Application	Method for enhance heat-mass transfer
Li et al. [52]	Experimental	BaCl–ammonia	Solar powered thermochemical cooling system	Composite block was produced by impregnating BaCl inside the graphite powder pores.
Liu et al. [53]	Experimental	CaCl ₂	Sorption thermal energy storage	SiO ₂ based mesoporous ceramic material is used. It is formed as honeycomb before CaCl ₂ is impregnated.
Cuyppers et al. [54]	Numerical	Zeolite	Seasonal thermochemical heat storage system	Zeolite spheres are in glued contact with a copper plate to obtain high thermal conductivity with low material usage.
Michel et al. [55]	Experimental–numerical	Salt powder–vermiculite	Developing high efficiency reactive bed for thermochemical heat storage	An experimental prototype is developed in order to modelling a high density reactive bed consists of salt.
Willers and Groll [56]	Experimental–numerical	Metal hydride	Designing and testing a two-stage metal hydride reactor	Helical copper band, which is helically soldered into the reactor was used as heat conduction matrix to increase thermal conductivity.
Klein et al. [57]	Experimental–numerical	Metal hydride	Designing hydride reactor consisted of four reaction beds.	Hydride powder was contained in aluminium-foam cylinders to improve heat and mass transfer
Lass-Seyoum et al. [58]	Experimental	Synthetic zeolites and composites (matrix of salthdrates/porous material)	Developed a long term thermochemical heat storage	Compared 3 types of heat exchangers to achieve the highest performance. 60% higher heat power rate achieved with the new exchanger configuration comparing with the standart heat exchangers in the bulk.
Österreich [59]	Experimental	Silica gel–water	Closed thermochemical storage for solar space heating	Storage volume filled with the storage material and equipped with an internal spiral heat exchanger for enhancing heat transfer.
Kerskes et al. [60]	Experimental	Zeolite	Solar thermal space heating with long-term sorption heat store	Zeolite honeycomb monoliths is used for increasing sorption characteristics and decreasing pressure drop during air flow.
Kerskes et al. [61]	Experimental	Packed bed zeolite spheres	Thermochemical heat storage for solar thermal applications	Sorption store is divided in several segments which can be desorbed or adsorbed separately in small amounts for decreasing heat losses
Kerskes et al. [62]	Experimental	Zeolite and salt	Thermochemical heat storage	An external reactor concept has been realized where the storage material is separated from the reactor. This has the advantage that the reaction is reduced to only a small part of the total storage material amount at a time. The thermal heat capacities and heat losses especially during the regeneration process are reduced
Restuccia et al. [63]	Experimental	Zeolite	Thermochemical heat storage reactor	Dip coated adsorbents made of SAPO-34 zeolite on a finned flat-tube aluminum heat exchanger was prepared
Yang et al. [64]	Numerical	Metal hydride	Thermochemical heat pump	Packed bed reactor design
Bao et al. [65]	Numerical	Metal hydride	Thermochemical heat storage reactor storage reactor	Heat exchanger optimization for metal hydride thermal energy storage reactor has been made
Schaube et al. [66]	Numerical–experimental	Calcium hydroxide Ca(OH) ₂	Thermochemical heat storage reactor	Thermal behavior of a reactor with direct heat transfer between the gaseous reactant and the solid material was investigated
Hirata et al. [67]	Numerical–experimental	CaCl ₂ –expanded graphite	Adsorbent materials	Composite particles of Calcium chloride with expanded graphite and methylamine is used as reactants. Reaction and heat transfer characteristics of the composite particles was investigated experimentally in a thin packed bed reactor and confirmed with numerical solutions
Tian et al. [68]	Experimental	CaCl ₂ –activated carbon-expanded graphite	Adsorbent materials	Heat and mass transfer performance of compact chemical and physical absorbents is investigated.
Jiang et al. [69]	Experimental	Eight different salts and expanded natural graphite as the host matrix	Adsorbent materials	Various types of adsorbents is designed and their performances were compared in order to enhance heat and mass transfer potentials.
Mauran et al. [70]	Experimental	SrBr ₂ –H ₂ O	Thermochemical heat storage reactor	Solid/gas thermochemical heating–cooling reactor is developed

of LiCl. This condition provides a significant decrease of salt solvation from the matrix component. On the other hand, increasing the LiCl percentage results in the formation of two solid phases which are the solution of LiBr in LiCl, and the solution of LiCl in LiBr.

Molenda et al. [73] investigated the hydration and dehydration behaviours of CaCl₂ at different partial vapour pressures. The reversibility, reaction steps and stability of CaCl₂ was also reported. According to the experimental results the researchers showed that the hydration reaction provides good reversibility and stability for ≈ 20 cycles and the results appear to be in good agreement with the literature.

Balasubramanian et al. [74] developed a mathematical model to investigate the capability of salt hydrates to store thermochemical energy during their dissociation into anhydrous salts and water with an external heat supply. They reported that the heat supplied

for desorption is gradually absorbed by the anhydrous salt and results in an increase of desorption duration with an associated increase of heat loss to the environment. It is indicated that the process performance may be improved by using materials that have higher thermal conductivities, higher specific heat capacities and lower thermochemical desorption rates.

2.5. Selected Studies on thermochemical heat storage process design

Zondag et al. [75] constructed a prototype thermochemical sorption heat storage system at the Energy Research Centre of The Netherlands. It is a packed bed sorption system which contains 17 dm³ of the sorption material (MgCl₂ · H₂O). They reported that an effective storage density of 0.5 GJ/m³ was obtained from the system. It was also reported that the sorption material is capable

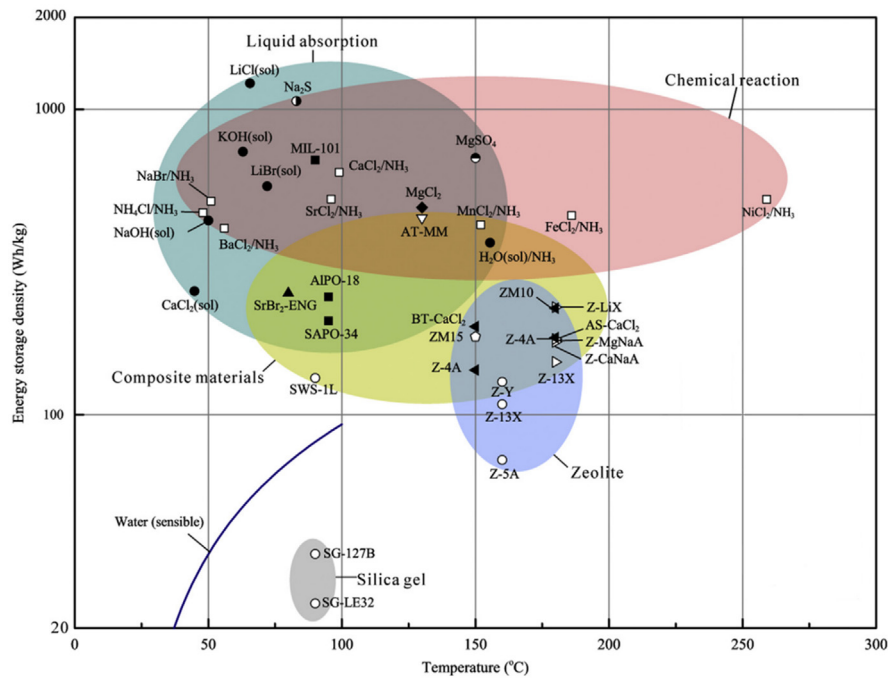


Fig. 7. Energy storage densities of sorption materials [26].

Table 6

Performance comparison of different configurations [76].

	Closed circuits	Open circuit with humidifier	Open circuit	Open circuit with recirculation
Components (in addition to fan, reactor, air–water exchanger)	Humidifier	Air–air heat exchanger humidifier	Air–air heat exchanger	Air–air heat exchanger recirculation
COP	11	9.6	8.2	6.8
Productivity rate (%)	37	53	80	90

of generating 150 W of thermal power for 40 h with an airflow of 410 l/min with a vapour pressure of 12 mbar. However as a result of heat losses only 50 W could be transferred to the load resulting in a system COP of 12.

Tanguy et al. [76] conducted a parametric study to evaluate the impact of both the internal (air flow rate, heat exchanger pressure drop) and external conditions (outdoor temperature) on the performance of a THS system. Two parameters are taken into consideration for the performance analysis. These are the COP (useful energy/electrical energy consumption) and productivity rate (useful energy/reaction discharged energy). A strontium bromide reactor with an external air–water heat exchanger was used in the study. The researchers reported that the THS system had to be studied in three parts; (i) material, (ii) reactor and (iii) process. Four experimental setups were used as part of the study: (i) closed circuit, (ii) open circuit, (iii) open circuit with humidifier open and (iv) open circuit with recirculation. These different working scenarios have been compared in terms of COP and productivity rate. The experimental results are given in Table 6.

In another experimental study, Mette et al. [77] developed a highly efficient regeneration process for a THS system. A zeolite based composite material was used as the absorbent. It was reported that drying the air flow before entering the reactor significantly reduced the required regeneration temperature, T_r . Using the simulation software TRNSYS to analyse the regeneration temperature, it was found that T_r could be decreased from 180 °C to 130 °C, which approaches suitable temperatures for utilizing solar energy. The researchers developed a model for thermo-

economic performance of the system called fractional energy saving (f_s). Here, f_s is the comparison of auxiliary energy demand of the solar heating system to the energy demand of conventional heating (non-solar) system. It was found that, utilizing this system coupled with moderate collector sizes ($> 20 \text{ m}^2$) could provide a fractional energy saving of $f_s > 60$ when compared with a more conventional regeneration processes.

Abedin and Rosen [78] investigated both closed and open THS systems using energy and exergy analysis methods to evaluate the charging behaviour and overall cycle performance of their system (see: Fig. 8a–c). The energy and exergy efficiency of the systems were determined as 50% and 9% for the closed storage and 69% and 23% for the open storage respectively.

Stitou et al. [79] carried out an experimental investigation of a solar assisted THS system used for air conditioning in a pilot plant for housing in France. The plant, which has a daily cooling capacity of 20 kW h, consists of a solid–gas thermochemical sorption process which is assisted at 60–70 °C by 20 m² of flat plate solar collectors. The reactive solid BaCl₂ and a phase change refrigerant, NH₃ were used as the sorption couple. It was reported that over a period of two years the average efficiency of the solar collectors was found to be ≈ 40 –50% whilst the process COP was ≈ 30 –40%. It was shown that with this prototype system a 0.8–1.2 kW cooling load per m² of flat plate solar collector could be supplied.

There are several other studies into both open and closed THS systems used for various purposes with some of these are listed in Table 7. The materials used, storage type, method and analysis results are shown. It is clear from the comprehensive spread

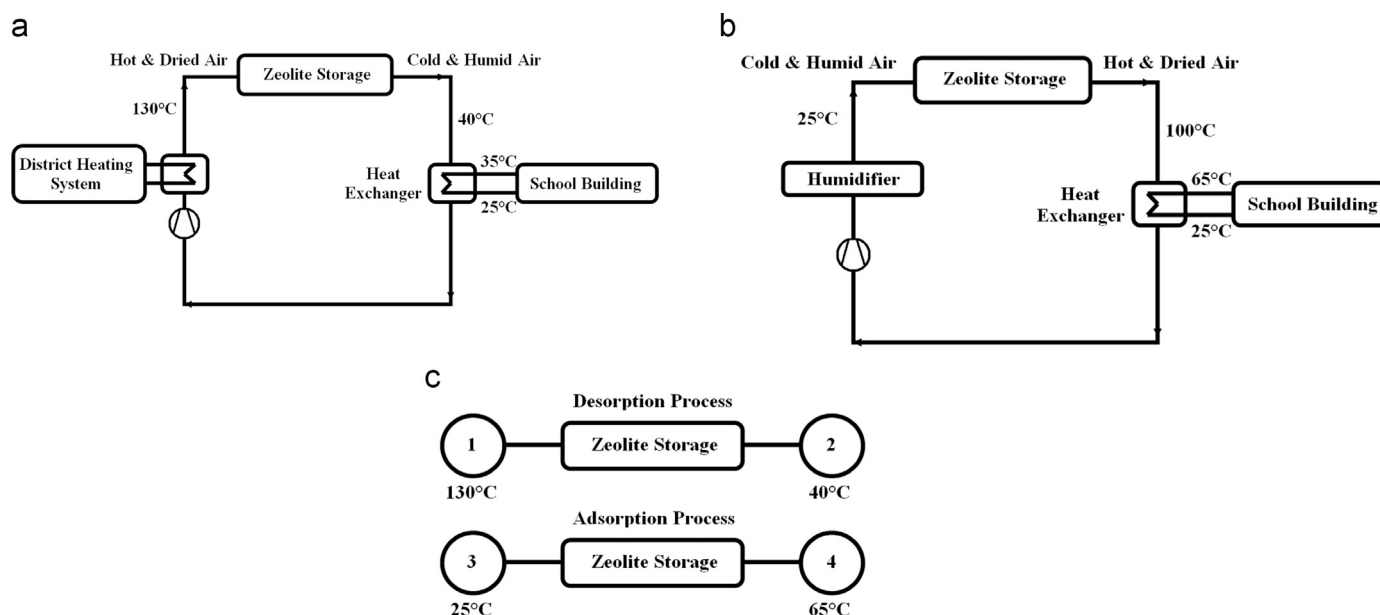


Fig. 8. (a) Zeolite THS charging (desorption) – closed cycle [78]. (b) Zeolite THS discharging (adsorption) – closed cycle [78]. (c) Adsorption and desorption processes – open cycle [78].

Table 7

Previous studies on THS.

	Concept	Material	Type of study	Storage method	COP	Heat storage density
Zondag et al. [75]	Open THS	MgCl ₂ –H ₂ O	Experimental	Short term	12	50 W
Li et al. [80]	Dual mode THS	CaCl ₂ –NH ₃	Numerical	Seasonal	0.6	1043 kJ/kg
Stitou et al. [79]	Solar assisted solid/gas THS	BaCl ₂ –NH ₃	Experimental	Short term	0.3–0.4	0.8–1.2 kW h
Tanguy et al. [76]	Optimization of THS for solar app.	SrBr ₂	Numerical	Seasonal	6.8–11	–
Le Pierres et al. [81]	THS for solar deepfreezing	BaCl ₂ –NH ₃	Experimental	Seasonal	0.031	–
Li et al. [82]	Comparison of adsorption and resorption THS	BaCl ₂ –NH ₃ MnCl ₂ –NH ₃	Experimental	Seasonal	0.78(ads.) 0.46 (res.)	–
Bao et al. [83]	THS for cold storage and refrigeration	MnCl ₂ –NH ₃ NH ₄ Cl–NH ₃	Experimental	Short term	0.3–0.31	87–125 W/kg _{salt}
Basciotti and Pol [84]	THS for cooling application	Silica gel	Numerical	Seasonal	0.61–0.84	9.7–12.1 kW
Bales et al. [85]	THS	Zeolite	Experimental	Seasonal	–	57.8 kW h/m ³
De Boer et al. [86]	Solid sorption cooling integrated THS	Na ₂ S	Experimental	Seasonal	0.57	2.1 kW h
Li et al. [87]	Deep freezing application	MnCl ₂	Experimental	Seasonal	0.34	350 W/kg
Oliviera et al. [88]	Air conditioning	NaBr	Experimental	Seasonal	0.46	129 W/kg
Chen et al. [89]	Air conditioning	BaCl ₂	Experimental	Seasonal	0.5	192 W/kg
Vaselovskaya et al. [33]	Air conditioning	BaCl ₂	Experimental	Seasonal	0.54	370–500 W/kg
Vasiliev et al. [90]	Refrigeration	CaCl ₂	Experimental	Seasonal	0.43	–
C. Wang et al. [91]	Heat transformation	CaCl ₂ –MnCl ₂	Experimental	Seasonal	0.25	248 W/kg
Fadhel et al. [92]	Drying application	CaCl ₂ –NH ₃	Experimental	Seasonal	1.2–2	–
Haije et al. [93]	Heat transformation	LiCl–MgCl ₂	Experimental	Seasonal	0.11	222 W/kg
Van Essen et al. [94]	Heat storage	AlSO ₄ , CaCl ₂	Experimental	Seasonal	–	–
Lahmidi et al. [95]	Heating and Cooling	Sr Br ₂	Experimental	Seasonal	–	26 W/kg (h)–49 W/kg (c)
Mauran et al. [70]	Heating and Cooling	SrBr ₂	Experimental	Seasonal	–	13 W/kg (h)–15 W/kg (c)
Carkvenik et al. [96]	Three stage cascade sorption refrigeration	LiBr–H ₂ O CaO–H ₂ O	Experimental	Seasonal	1.8	–
Ruiter JP [97]	Closed CHP	NH ₃ –H ₂ O	Experimental	Seasonal	–	119 kW h/m ³
Bales et al. [98]	Closed CHP	NaOH–H ₂ O	Experimental	Seasonal	–	250 kW h/m ³
Quinnell et al. [99]	Closed CHP integrated with heat storage	CaCl ₂	Experimental	Seasonal	–	381 kW h/m ³
N'Tsoukpoe [100]	Long-term solar thermal storage	LiBr–H ₂ O	Experimental	Seasonal	–	8 kW h
Lu et al. [101]	Closed THS	Zeolite 13 ×	Experimental	Seasonal	–	167 kW h/m ³
Hauer et al. [102]	Open THS	Zeolite 13 ×	Experimental	Seasonal	–	124 kW h/m ³

of usage that THS can be used in wide range of applications, including heat storage, air conditioning, cold storage, deep freezing, drying and heat transformation purposes.

2.6. Thermochemical heat storage: an alternative for heat pumps

THS systems have excellent energy storage densities when compared with other heat storage methods. However vapour

transfer to the adsorbent during discharging and heat transfer during charging remain the main obstacles to the successful implementation of these systems. The complexity of the HAM transfer problem can serve to limit the heat storage volume. Due to this, generation of heat over longer periods of time with high temperatures is still open for improvement. One alternative technology to successfully utilize the heat from 'open' THS systems would be to combine them with a heat pump (HP). The

temperature of the heated output air from the reaction unit is approximately 35–40 °C. This temperature range is not enough to provide adequate comfort conditions in buildings except when using wall or ground radiating heating technologies. If however, the heat generated by a THS system is fed into a low temperature heat source HP, it would increase the efficiency of both systems. As the heat input to the HP evaporator increases (compared with air sourced heat pump), the energy consumption in its compressor will drop and thus the COP will increase. Solar or ground source heat is highly dependent on the local weather conditions and fluctuations of the temperature can hamper system design. The heat generation from a THS system is inherently more stable and it is therefore much better suited as the input source for a HP. In addition to this efficiency improvement, the waste heat from the HP during its cooling mode (in the summer period) can also be used for regeneration of the THS system further increasing efficiency.

3. Conclusions

A comprehensive review of THS has been presented. Technology used for CHP, adsorption and absorption cycles, adsorbate/adsorbent and absorbate/absorbent couples are investigated. Some key applications of absorbent materials are also presented. It is seen that the air flow rate, ambient temperature, relative humidity and the design of the reactor are the most promising factors in obtaining significant performance from THS systems.

Recent research focus on several absorption and adsorption pairs has been presented. The most desirable properties of THS materials have been shown to be (i) high energy density, (ii) low charging temperature, (iii) high thermal conductivity, and (iv) high sorbate uptake. Further research is needed on many aspects of THS design including (i) materials, (ii) reactor design factors, (iii) safety, (iv) size and (v) efficiency and economics. In addition to this, comprehensive performance analysis of these systems, based on their energy and exergy are required in order to obtain an advanced and capable THS systems.

A primary result of this review concludes that although many research studies are ongoing, THS technology is still not at a sufficiently developed stage for commercialisation. The factors outlined below should be taken into consideration in order to achieve both an efficient and economically feasible THS system:

1. Reactor design – effective HAM transfer is vital for THS efficiency. To achieve a high output temperature for a sufficiently long time period, a high quantity of material must be available for that reaction. Achieving full reaction is also dependant on the interaction between the reactant materials.
2. Materials study – developing new composite materials with higher storage density, low regeneration temperature, good cyclic ability and low price is crucial.
3. Humidification process – as the heat generation from most THS systems are relatively low, energy consumption to run them should be minimal to achieve sufficient system efficiency. For this reason, in particular for large scale applications, research into development of new humidification systems with very low energy consumption is highly important.
4. Regeneration process – utilization of solar energy in the summer period for charging THS systems would make seasonal storage possible. However the high regeneration temperature requirement of adsorbents (especially materials with high storage density) is still the main obstacle to benefitting from solar systems. Research into hybrid processes where solar collectors coupled with THS heat pumps are integrated and

optimized should be carried out together to improve the performance of THS.

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